

AD 749 820

OFFICE OF NAVAL RESEARCH

Contract N00014-67-A-0151-0024

Task No. NR 356-504

Technical Report No. 11

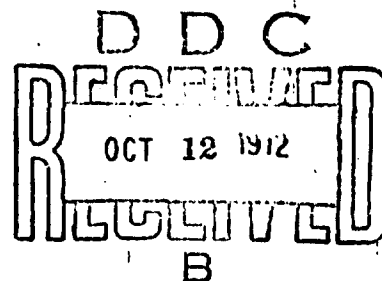
HIGH TEMPERATURE ELASTOMERS: THERMO-OXIDATIVE
BEHAVIOR OF A SYSTEMATIC SERIES OF LINEAR POLY(CARBORANE-
SILOXANE)S CONTAINING ICOSAHEDRAL $-CB_{10}H_{10}C-$ CAGES

by

J. K. Gillham and M. B. Roller

Submitted for publication in the
Journal of Applied Polymer Science

Princeton University
Polymer Materials Program
Chemical Engineering Department
Princeton, New Jersey 08540

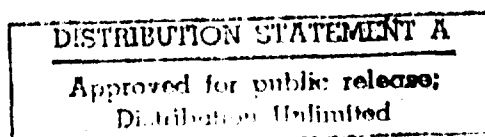


June 1972

Reproduction in whole or in part is permitted for any purpose
of the United States Government

Distribution of this report is unlimited

NATIONAL TECHNICAL
INFORMATION SERVICE



Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D

Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified

ORIGINATING ACTIVITY (Corporate author)

Princeton University
Princeton, N. J.28. REPORT SECURITY CLASSIFICATION
Unclassified

29. GROUP

3. REPORT TITLE

High Temperature Elastomers: Thermo-Oxidative Behavior of a
Systematic Series of Linear Poly(carborane-siloxane)s Containing
Icosahedral -CB₁₀H₁₂C- Cages.

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Technical Report Number 11

5. AUTHOR(S) (First name, middle initial, last name)

John K. Gillham and Mark B. Roller

6. REPORT DATE

June 1972

7a. TOTAL NO. OF PAGES

22

7b. NO. OF REFS

6

8. CONTRACT OR GRANT NO.

N00014-67-A-0151-0024

9a. ORIGINATOR'S REPORT NUMBER(S)

TR No. 11

9. PROJECT NO.

NR 356-504

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned
this report)

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale;
its distribution is unlimited.

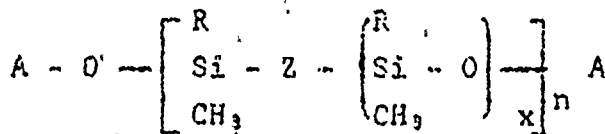
11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

Office of Naval Research
Washington, D. C.

13. ABSTRACT

A study of oxidative instability versus molecular structure for a systematic series of well defined linear poly(carborane-siloxane)s is reported. These polymers form the backbone components of the most recently developed high temperature elastomers. The basic structure is



where 1) $x=1,3,4,5,\infty$; 2) A=end-groups (reactive and inert); 3) Z=meta-, para-carborane (for $x=3$); 4) R= $-CH_3$, R= $-C_2H_5$, CF₃ (for $x=3$); one in five R= $-C_6H_5$ with the remainder $-CH_3$ (for $x=4$); 5) molecular weight = $\sim 10,000$; $\sim 55,000$ (for $x=3$). Thermomechanical spectra in air (~ 1 cps) from $130^\circ C$ to $625^\circ C$ at $3.6^\circ C/min$, thermogravimetric data from $25^\circ C$ to $600^\circ C$ in air ($3.6^\circ C/min$) and differential thermal data from $25^\circ C$ to $450^\circ C$ in air ($15^\circ C/min$) are presented. Thermo-oxidative stability is discussed in terms of structure and broad categories of behavior are defined.

DD FORM 1473 (PAGE 1)

NOV 65
54 0101-807-6801

Unclassified

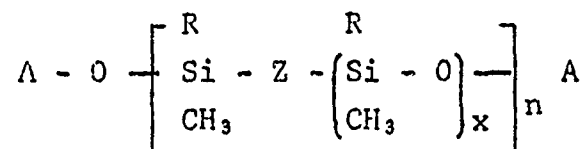
Security Classification

Security Classification

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Thermomechanical Spectra	2,7					
Torsional Braid Analyzer	8,10					
Mechanical Hysteresis	7					
Transition Regions	2					
Controlled Atmosphere	5					
Poly(carborane-siloxane)s	1					
Oxidative Cure	5,6					

ABSTRACT

A study of oxidative instability versus molecular structure for a systematic series of well defined linear poly(carborane-siloxane)s is reported. These polymers form the backbone components of the most recently developed high temperature elastomers. The basic structure is:



where 1) $x = 1, 3, 4, 5, \infty$; 2) Λ = end-groups (reactive and inert); 3) Z = meta-para-carborane (for $x = 3$); 4) $R = -\text{CH}_3$, $R = -\text{C}_2\text{H}_4\text{CF}_3$ (for $x = 3$); one in five $R = -\text{C}_6\text{H}_5$ with the remainder $-\text{CH}_3$ (for $x = 4$); 5) molecular weight = $\sim 10,000, \sim 50,000$ (for $x = 3$). Thermo-mechanical spectra in air (~ 1 cps) from $130^\circ\text{C} \rightarrow 625^\circ\text{C} \rightarrow 130^\circ\text{C}$ at $3.6^\circ\text{C}/\text{min}$, thermogravimetric data from $25^\circ\text{C} \rightarrow 800^\circ\text{C}$ in air ($3.6^\circ\text{C}/\text{min}$) and differential thermal data from $25^\circ\text{C} \rightarrow \sim 450^\circ\text{C}$ in air ($15^\circ\text{C}/\text{min}$) are presented. Thermo-oxidative stability is discussed in terms of structure and broad categories of behavior are defined.

HIGH TEMPERATURE ELASTOMERS : THERMO-OXIDATIVE
BEHAVIOR OF A SYSTEMATIC SERIES OF LINEAR
POLY(CARBORANE-SILOXANE)S CONTAINING ICOSAHEDRAL
-CB₁₀H₁₀C- CAGES.

M. R. Foller and J. K. Gillham

Polymer Materials Program
Department of Chemical Engineering
Princeton University
Princeton, N. J. 08540

INTRODUCTION

Recently the thermomechanical properties of a systematic series of linear poly(carborane-siloxane)s containing icosahedral -CB₁₀H₁₀C- cages were reported(1). The report included physical properties of the materials (melting, crystallization, glass and glassy state secondary transitions) as determined by torsional braid analysis (TBA). It also reported a high degree of thermal stability (in nitrogen and argon) as detected by TBA, thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The data indicated that in nitrogen, at a heating rate of 26 deg C/min, several of these materials did not crosslink

or lose appreciable weight until temperatures greater than 500deg.C. Expanding upon the previous report, this communication discusses the thermo-oxidative stability of the linear polymers in mechanical (by TBA) and thermal (by DTA and TGA) terms.

EXPERIMENTAL

Materials: The structures of the systematic series of linear carborane-siloxane polymers studied herein are shown in Table 1.

Techniques: The thermomechanical spectra (Figures 1-3) were determined by torsional braid analysis (2,3,4). The spectra, in flowing air, cover the temperature range of 130 to 625 to 130deg.C at a programming rate of 3.6deg.C/Min. The specimens were solution-cast , glass braid/polymer composites. All of the specimens, except 10-SiB-1, were prepared by drying (in nitrogen at 2 deg C/Min to 200deg.C) a braid soaked in a 10 percent (g polymer/ ml solvent) solution of polymer in benzene. The 10-SiB-1 material was virtually insoluble in refluxing xylene. The 10-SiB-1 specimen was prepared from a 5 percent slurry in refluxing xylene and was dried in nitrogen to 280deg.C at 2 deg.C/Min

The TGA curves (Figures 1-3) were generated on a

du Pont 950 thermogravimetric analyzer. The specimens were cast from the same solutions used to make the mechanical specimens and were run at 3.6 deg.C/Min. About 75mg of solution were used for each run. Larger specimen weights (about 120mg solution) gave somewhat different results, which will be discussed later.

The DTA curves (Figures 4-6) were generated on a du Pont 900 thermoanalyzer. The specimens were bulk polymers taken as received. The heating rate was 15deg.C/Min.

In all the experiments, bottled inhalator air was used (one bottle for all the mechanical work and one for all the TGA and DTA work). The air was specified at 10 parts per million moisture.

RESULTS AND DISCUSSION

The 10-SiB-X series: This series includes polymers I, IV, VII, XI and XII of Table 1. The TGA data and the TBA relative rigidity data are in Figure 1; the DTA data are in Figure 4.

The 10-SiB-X TGA data indicate that, with the exception of pure silicone (10-SiB- ∞ , XII), these materials are thermogravimetrically stable. The onset of weight loss was about 300deg.C for all these polymers. Above 350deg.C all

the carborane polymers started to gain weight and at about 525 deg C all but 10-SiB-1 lost weight again. The latter temperature corresponds to the only region of weight loss for these materials in an inert atmosphere (1). The curves for IV and VII were different when larger samples were used (about 120mg). In each case the increase in weight above 350 deg.C did not occur, although all other features remained intact. It is of interest to note that there appears to be no simple relationship between the degree of weight loss by 800 deg.C and the number of siloxane linkages per repeat unit. A linear relationship was found for the weight loss by 800 deg.C in argon(1). 10-SiB-1 seems the most oxidatively stable when examined via TGA

The 10-SiP-X DTA data revealed the melting point for 10-SiB-1 as a sharp endotherm. All the 10-SiB-X polymers began to enter broad exothermic peaks in the range of 225 to 250 deg.C. With the exception of 10-SiB-4, the first peak occurred at higher temperatures when more siloxane groups were in the repeat unit. A further sharp well defined exotherm was present between 300 and 425 deg.C; again the peak temperatures increased with siloxane content. The data was bouncy and not reproducible above approximately 430 deg C (this part is not shown) indicating a violent reaction

The 10-SiB-X TBA relative rigidity curves are in Figure 1. All of the carborane-containing polymers experienced a mode of stiffening near 300 deg.C. The 10-SiB-1, 3, 4 and 5 polymers commenced stiffening at 300, 290, 290 and 270 deg.C respectively. The 10-SiB-3, 4 and 5 polymers gave virtually identical stiffening plots from 300 to about 400 deg.C, while 10-SiB-1 was shifted somewhat to higher temperatures (about 25 deg.C). Examining the data from the point of view of the inflection point of the rigidity rise, all the carborane polymers had this point at about 360 deg.C. Pure silicone was considerably more stable from an oxidative-mechanical point of view since it began to stiffen at about 350 deg.C and had an inflection temperature of about 405 deg.C. The rigidity decreased above 400 deg.C for all the carborane polymers and above 540 deg.C it increased again. The maximum in the rigidity curve could indicate that there was a scission reaction competing successfully with the stiffening reaction or that the new material formed during the initial stiffening process was experiencing a physical transition (e.g. Tg). On the other hand, the pure silicone experienced only a one stage stiffening process. The temperature for the maximum in rigidity for the carborane polymers seems to correspond to the temperatures of the final sharp exotherm seen by DTA in all

cases except 10-SiB-1. This would indicate that a reactive softening mechanism is more likely than a physical one (e.g., Tg). On cooling from 625 deg.C, all the carborane polymers appeared to have broad glass transitions between 400 and 500 deg.C [The rigidity level, after curing to 625 deg.C, was dependent upon the fraction of polymer on the braid (braid loading)]. This type of behavior has been reported for other carborane-siloxane polymer systems which contained both B₁₀ and B₅ cages (5). The 10-SiB-X polymers began to stiffen at about the same temperature as the 5-SiB-1 polymer previously reported (5), but at a lower temperature than the 5-SiB-1, 20 mole percent 10-SiB-1 copolymer discussed therein (the higher temperature of oxidative degradation for the B₁₀/B₅ copolymer may have been due to the presence of catalyst residue ferric ion impurities acting as oxidative stabilizers). Pure silicone appears the most oxidatively stable by both DTA and TBA studies.

The 10-SiB-3 series: This series includes polymers IV-VI of Table 1. The TGA data and the TBA data are in Figure 2; the DTA data are in Figure 5.

The 10-SiB-3 TGA data indicate that all the methylated materials have a high degree of thermogravimetric stability and experienced the same multistep process seen in the

10-SiB-X series. The more organic fluorinated polymer (VI) did lose more than twice as much weight as the totally methylated polymers, with the first major weight loss region occurring near 350 deg. C. As in the 10-SiB-X series, all the methylated materials commenced weight loss at about 300 deg. C. The 10-SiB-3 para polymer had a final weight loss that was less than that for the meta-carborane polymers and the second stage of weight loss occurred about 40 deg. C higher. As before, the second stage weight loss in air for 10-SiB-3 para occurred at about the same temperature as the single stage weight loss in argon (*). The different weight loss levels for TV versus TT and TTT is most probably due to different molecular weight distributions (1). The 10-SiB-3 para appears to be the most oxidatively stable of the 10-SiB-3 polymers when studied by TGA, although the first temperature region of major weight loss was higher for the fluorinated polymer.

The 10-SiB-3 DTA data are very much like those for the 10-SiB-X series. The Tm's of TT, TTT and V were revealed by sharp endotherms at 47, 47, and 108 deg. C, corresponding well to the reported values(1). A two-stage process commencing between 225 and 250 deg. C, except for the fluorinated polymer which entered an exotherm at about 300 deg. C, was indicated for all polymers. The first stage of

the exotherm for the fluorinated material was flatter than for the other 10-SiB-3 polymers, and the second exotherm peaked at 440 rather than 390 to 410 deg.C. The more organic fluorinated material appears more oxidatively stable when examined by DTA.

The 10-SiB-3 TBA data are almost identical in form to those of the 10-SiB-X series, except for VT (the fluorinated polymer). All the methylated polymers experience the initial stiffening at about 280 deg. C and a maximum near 400 deg.C. The fluorinated polymer was similar except that the line of increase of rigidity was shifted to higher temperatures by about 25 deg.C and the maximum was at about 430 deg.C. All the methylated materials experienced a decrease in rigidity after the maximum and then stiffened again. The para-carborane polymer experienced the second stiffening about 40 deg.C higher (as with the second weight loss). The fluorinated polymer experienced two maxima indicating a three staged stiffening/softening process. All the materials again displayed a Tg region in the 400 to 500 deg.C range on cooling from 625 deg.C, as seen for the 10-SiB-X series. A ranking of thermomechanical oxidative stability is difficult to define within this series.

The 10-SiB-4 series: This series includes polymers VII, VIII and IX (VIII was not studied oxidatively). The TGA data

and the TBA data are in Figure 3; the DTA data are in Figure 6.

The 10-SiB-4 TGA data indicate a relatively high degree of thermogravimetric oxidative stability. The phenylated polymers (IX and X) displayed small total weight losses by 800 deg C, with the differences between them presumably being due to differences in molecular weight distributions and/or workup. The phenylated materials displayed a major mode of weight loss commencing at 350 deg.C rather than 300 deg C for 10-SiB-4. All three polymers displayed a weight gain (350 deg.C for VII, and 430 deg. C for IX and X) and the phenylated polymers displayed a broader region of weight gain. Only the totally methylated 10-SiB-4 experienced the second mode of weight loss common to the methylated polymers discussed above. In this series, the phenylated polymers are the most thermogravimetrically stable in air.

The 10-SiB-4 DTA data amplify the TGA results. Whereas the methylated 10-SiB-4 entered an exothermic region at about 240 deg.C, the phenylated polymers IX and X entered such a region at 300 and 290 deg.C respectively. The exotherms themselves reflected the less abrupt nature of the weight loss for the phenylated polymers. The exothermic peaks for the methylated 10-SiB-4 polymer were sharp, while those of the phenylated polymers were broad and diffuse.

The DTA data indicate high stability for the phenylated versus the totally methylated 10-SiB-4 polymers, both from the point of view of the onset of the oxidative exotherm and of the sharpness of the reaction region.

The 10-SiB-4 TPA data in Figure 3 include the plot of the 10-SiB- ∞ curve for comparison. The following ranking can be established for the three classes of materials in this figure. The phenylated carborane-siloxane polymers and the pure silicone are significantly more stable than the totally methylated 10-SiB-4, when monitored thermomechanically in air. Other interesting features are the 10 deg.C difference in the onset of catastrophic stiffening of the end-capped versus non-end-capped phenylated polymers (the end-capped reacts first as was detected via DTA), and the non-softening of the phenylated polymers above 400 deg.C. This second feature is of interest since the two-stage stiffening process was still evident. This stiffening is also complementary to the broad reaction peak detected by DTA. The phenylated materials appear to be more highly crosslinked than the other polymers (in all series) after the first stiffening process. This is apparent since all the other rigidity curves displayed very nearly the same value for relative rigidity at their respective maxima regardless of their braid loading. This

excess crosslink density may be due to the 430 deg.C stiffening observed thermally (in nitrogen) at the same programming rate (1), but not observed for the methylated polymers. On the other hand, the second stage of stiffening in all the polymers occurred near the temperature region (530 to 570 deg.C) of catastrophic stiffening in nitrogen (1).

None of the carborane polymer damping plots are shown because the data did no more than reflect the information derived from the rigidity plots. In general terms each damping curve displayed a damping peak corresponding to each stage of the multistaged stiffening region. On cooling from 625 deg.C a large drop in damping occurred at about 400 deg.C. The overall damping behavior was similar to that in air of the 5-SiB-1 polymers previously reported (5). Several of the materials which began to stiffen below 300 deg.C displayed a damping peak at the onset of stiffening and another one in the region of catastrophic stiffening. The others displayed only one peak corresponding to the first reaction region. Both types displayed further peaks at higher temperatures corresponding to the stiffening during later stages of reaction.

CONCLUSIONS

The thermo-oxidative studies discussed above, indicate

that the poly(carborane-siloxane)s listed in Table 1 fall into two classes of thermo-mechanical degradation. The first class, is composed of all the totally methylated carborane polymers (I-VII and XT), and is defined by the 280 to 300 deg C temperature region for the onset of stiffening. The second class, defined by a 350 deg.C onset of stiffening, is composed of pure silicone and the phenylated polymers. Examination of the TGA data for pure silicone would discount any advantage derived from the increased temperature of onset of stiffening, while the TGA data for the phenylated materials would indicate a high degree of relative utility. The two-step nature of the TGA data for all of the carborane polymers indicated that the response of the polymers in air was a combination of purely oxidative and purely thermal events that could be separated upon examination of previously reported thermomechanical data (1). The rather close grouping of the curves into the two reaction regions has prompted the authors to consider isothermal oxidative studies to better define the close ranking of the materials in each class and to determine activation energies for the stiffening process.

It is of interest to note that with respect to thermomechanical stability, the incorporation of carborane cages into siloxane backbones decreases the threshold of

oxidative stiffening. Related work reported recently in the Russian literature (6) indicated that the incorporation of m-carborane cages into polyamido backbones resulted in the formation of B_2O_3 upon long-term exposure to air at 230-250 deg.C. The oxidative attack of the carborane cage below 350 deg.C leading to crosslinks appears reasonable. The nature of the stiffening processes for the pure silicone (one step) versus the carborane polymers (multistep) and the transition behavior of the oxidatively cured materials ($T_g > 625$ deg.C for the silicone; $T_g = 400-500$ deg.C for the carborane polymers) further indicate that the carborane cage itself has some direct effect on the oxidation process. Future work to determine the chemical structure of the pyrolytic products of oxidation is planned in order to provide a better understanding of the degradation mechanism.

ACKNOWLEDGMENT

The support of the Office of Naval Research (contract No. N00014-67-A-0151-0024, NR 356-504) and the cooperation of Dr J. P. Sieckhaus of the Olin Research Center, New Haven, Ct is acknowledged.

REFERENCES

1. Poller, M. B. and Gillham, J. K., Thermomechanical behavior in nitrogen of a systematic series of linear

poly(carborane-siloxanes) containing $-CB_{10}H_{10}C-$ cages. Preprints, Division of Polymer Chemistry, Amer. Chem. Soc. 13, No. 1, 227 (1972).

2. Lewis, A. K., and Gillham, J. K., Novel technique for following the rigidity changes accompanying the curing of polymers. J. Appl. Polymer Sci., 6, 422, 1962.

3. Gillham, J. K., Torsional braid analysis. A semimicro mechanical approach to polymer analysis. Polymer Eng. and Sci., 7, No. 4, 225, 1967.

4. Gillham, J. K., and Roller, M. B., Advances in instrumentation and technique of torsional pendulum and torsional braid analyses. Polymer Eng. and Sci., 11, No. 4, 205, 1971.

5. Roller, M. B., and Gillham, J. K., Thermomechanical behavior of poly(carboranesiloxane)s containing $-CB_5H_5C-$ cages. Preprints, Division of Polymer Chemistry, Amer. Chem. Soc., 12, 600, 1971. Submitted for publication to J. Appl. Polym. Sci.

6. Korshak, V. V., Danilov, V. G., Komarova, I. G., Bekasova, V. I., and Leites, L. A., Thermal stability of poly(amido-m-carboranes). Vysokomol. Soedin. Ser. A 13(7), 1517 (1971).

TABLE CAPTIONS

Table 1 Structure and designation of 10-SiB polymers.

FIGURE CAPTIONS

Figure 1. Torsional braid and thermogravimetric analyses of 10-SiB-X polymers in air.

Figure 2. Torsional braid and thermogravimetric analyses of 10-SiB-3 polymers in air.

Figure 3. Torsional braid and thermogravimetric analyses of 10-SiB-4 polymers in air.

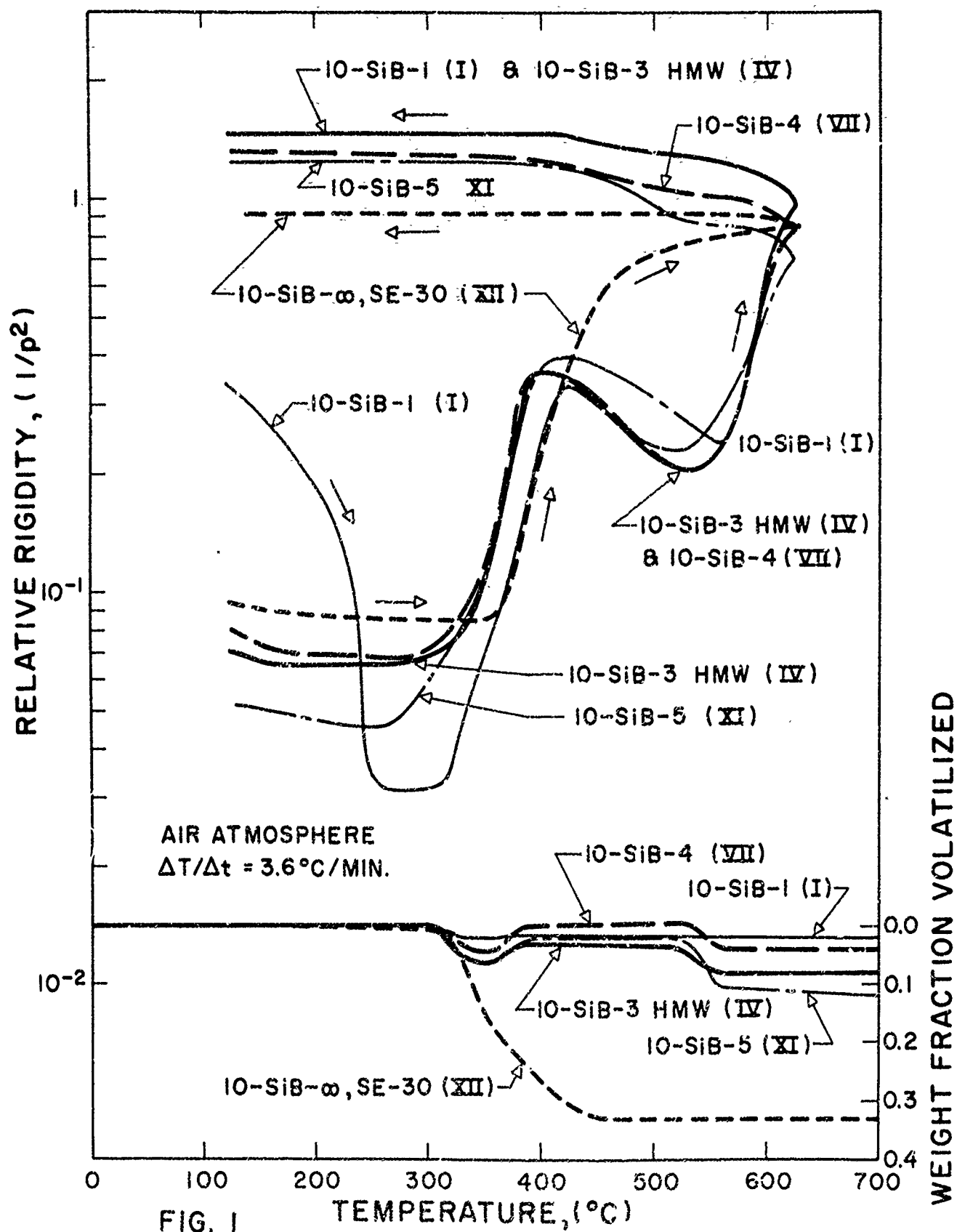
Figure 4. Differential thermal analysis of 10-SiB-X polymers in air.

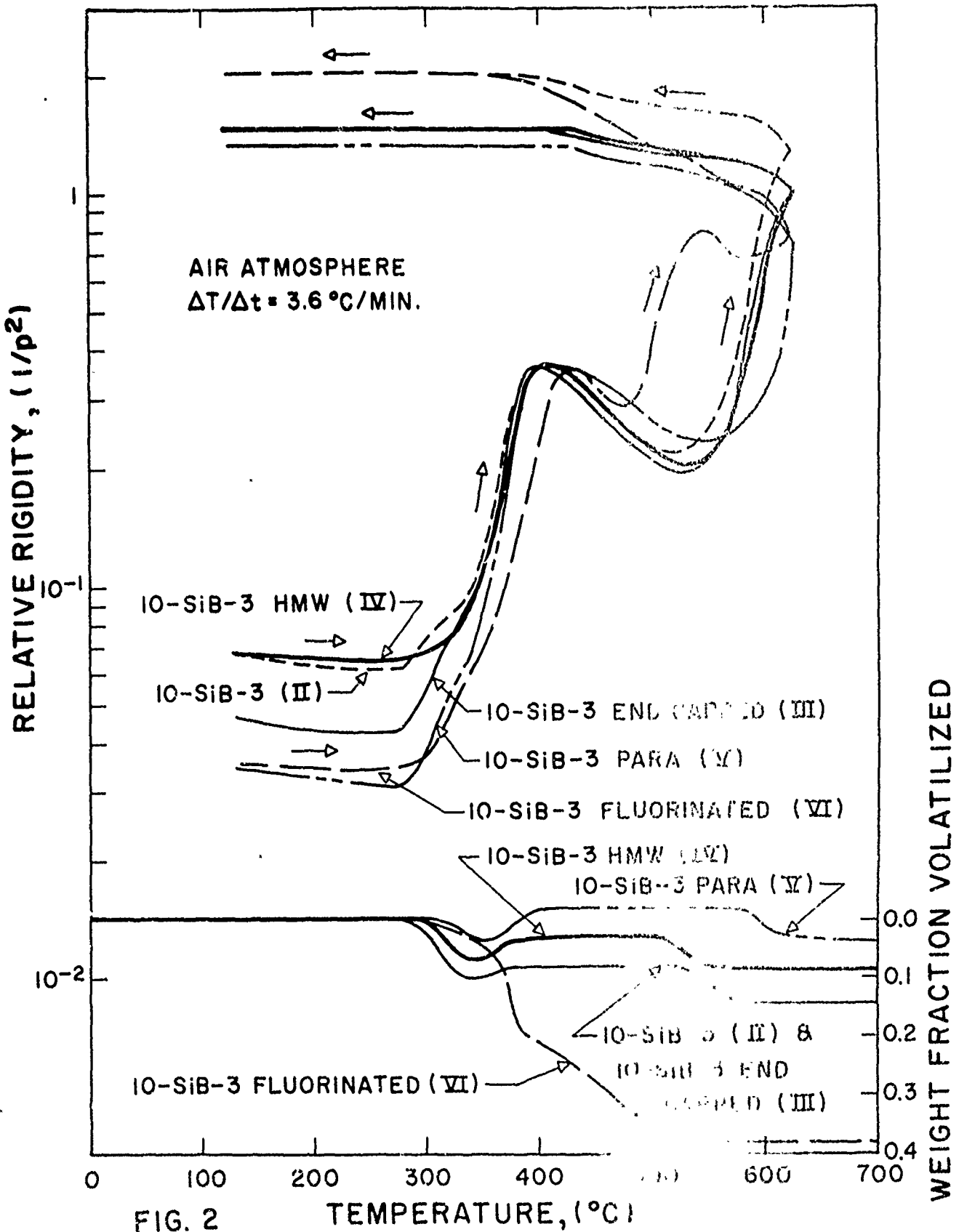
Figure 5. Differential thermal analysis of 10-SiB-3 polymers in air.

Figure 6. Differential thermal analysis of 10-SiB-4 polymers in air.

TABLE I

DESIGNATION	STRUCTURE
I 10-SiB-1	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{Si}-\text{CB}_{10}\text{H}_{10} \\ \\ \text{CH}_3 \end{array} \text{C} \begin{array}{c} \text{CH}_3 \\ \\ \text{Si}-\text{O} \\ \\ \text{CH}_3 \end{array} \right]_n \text{H}$
II 10-SiB-3	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \text{C} \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n \text{H}$ <p> $[\eta]_{\text{XYLENE}} = 0.15-0.20 \text{ dl/g}$ GPC PEAK MAX ~ 10-12,000 </p>
III 10-SiB-3 END-CAPPED	$\text{CH}_3-\text{Si}-\text{O}-\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \text{C}-\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \text{Si}-\text{CH}_3$ <p> $[\eta]_{\text{XYLENE}} = 0.15-0.20 \text{ dl/g}$ MADE FROM II </p>
IV 10-SiB-3 HIGH MW	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \text{C} \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n \text{H}$ <p> $[\eta]_{\text{XYLENE}} = 0.65 \text{ dl/g}$ MW ~ 50-100,000 </p>
V 10-SiB-3 PARA	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{C}_6\text{H}_4 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \text{C} \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n \text{H}$ <p>GPC PEAK MAX. ~ 15,000</p>
VI 10-SiB-3 FLUORINATED	$\text{HO} \left[\begin{array}{c} \text{CF}_3 \quad \text{CF}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \text{C} \begin{array}{c} \text{CF}_3 \quad \text{CF}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n \text{H}$ <p>GPC PEAK MAX. ~ 8,500</p>
VII 10-SiB-4	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \text{C} \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O} \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n \text{H}$ <p>GPC PEAK MAX. ~ 24,000</p>
VIII 10-SiB-4 ϕ RANDOM	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \text{C} \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_{0.5} \left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{Si}-\text{O} \\ \\ \text{CH}_3 \end{array} \right]_{0.5} \text{H}$ <p> $M_n = 12,000$ GPC PEAK MAX. ~ 15-20,000 RANDOM COPOLYMER </p>
IX 10-SiB-4 ϕ	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \text{C} \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{C}_6\text{H}_5 \\ \quad \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O} \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n \text{H}$ <p>GPC PEAK MAX ~ 12-18,000</p>
X 10-SiB-4 ϕ END-CAPPED	$\text{CH}_3-\text{Si}-\text{O}-\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \text{C}-\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{C}_6\text{H}_5 \\ \quad \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O} \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \text{Si}-\text{CH}_3$ <p> GPC PEAK MAX ~ 12-18,000 MADE FROM IX </p>
XI 10-SiB-5	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10} \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \text{C} \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O} \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n \text{H}$ <p>GPC PEAK MAX ~ 20,000</p>
XII 10-SiB- ∞ SE-30	$\text{CH}_3-\text{Si}-\text{O}-\begin{array}{c} \text{CH}_3 \\ \\ \text{Si}-\text{O} \\ \\ \text{CH}_3 \end{array} \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{Si}-\text{O} \\ \\ \text{CH}_3 \end{array} \right]_n \text{Si}-\text{CH}_3$ <p>MW > 10^6</p>





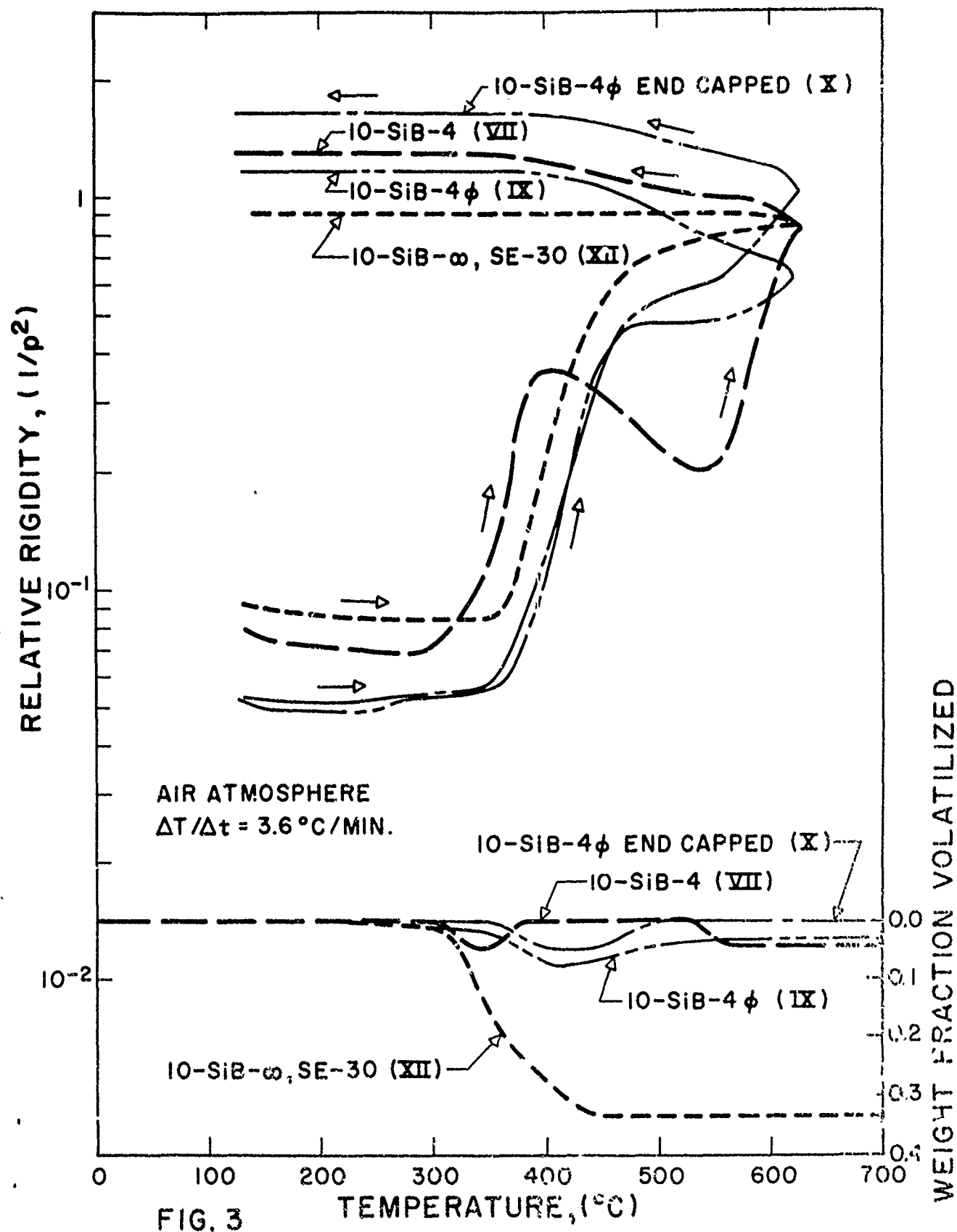
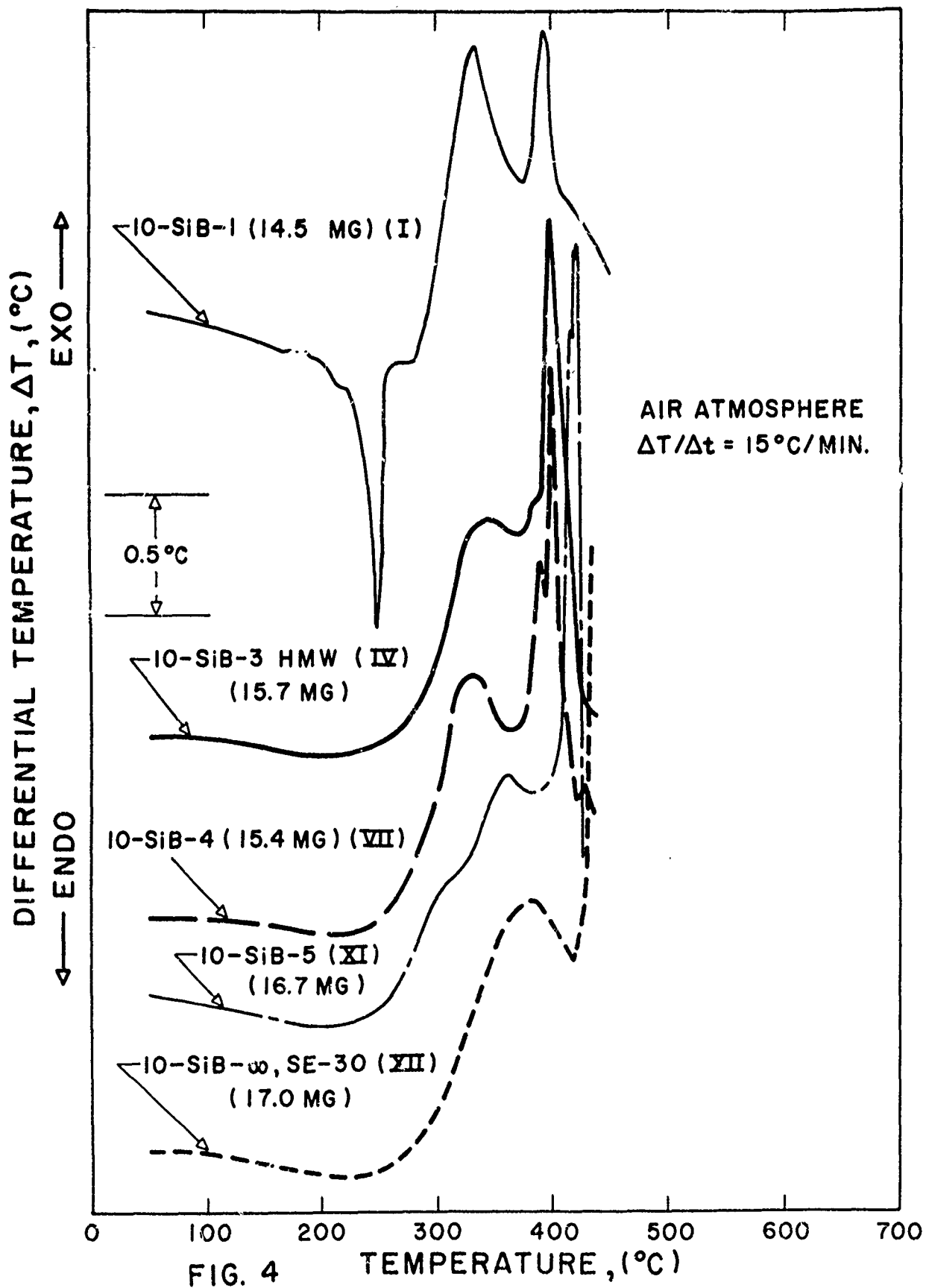


FIG. 3



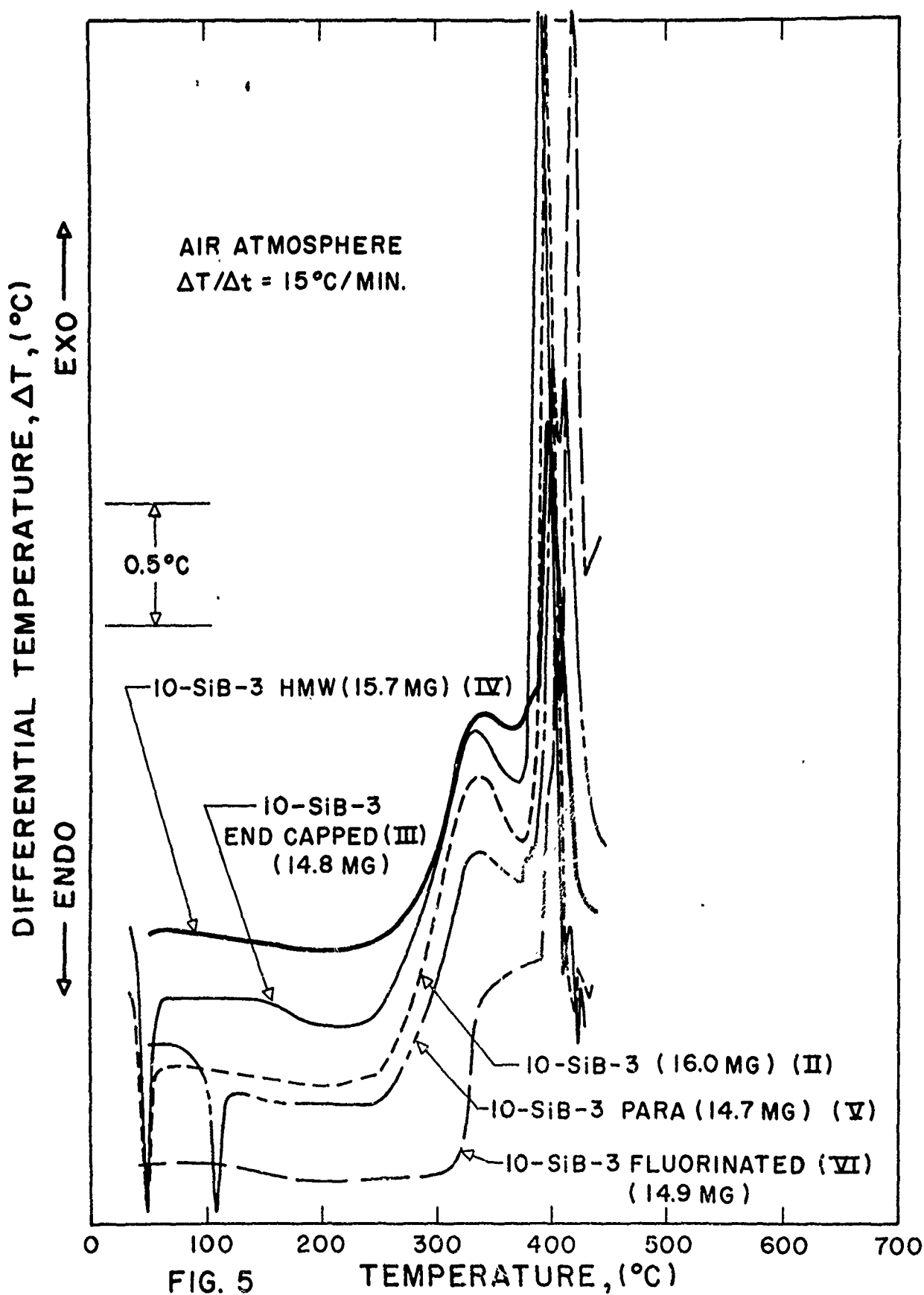


FIG. 5

TEMPERATURE, ($^{\circ}\text{C}$)

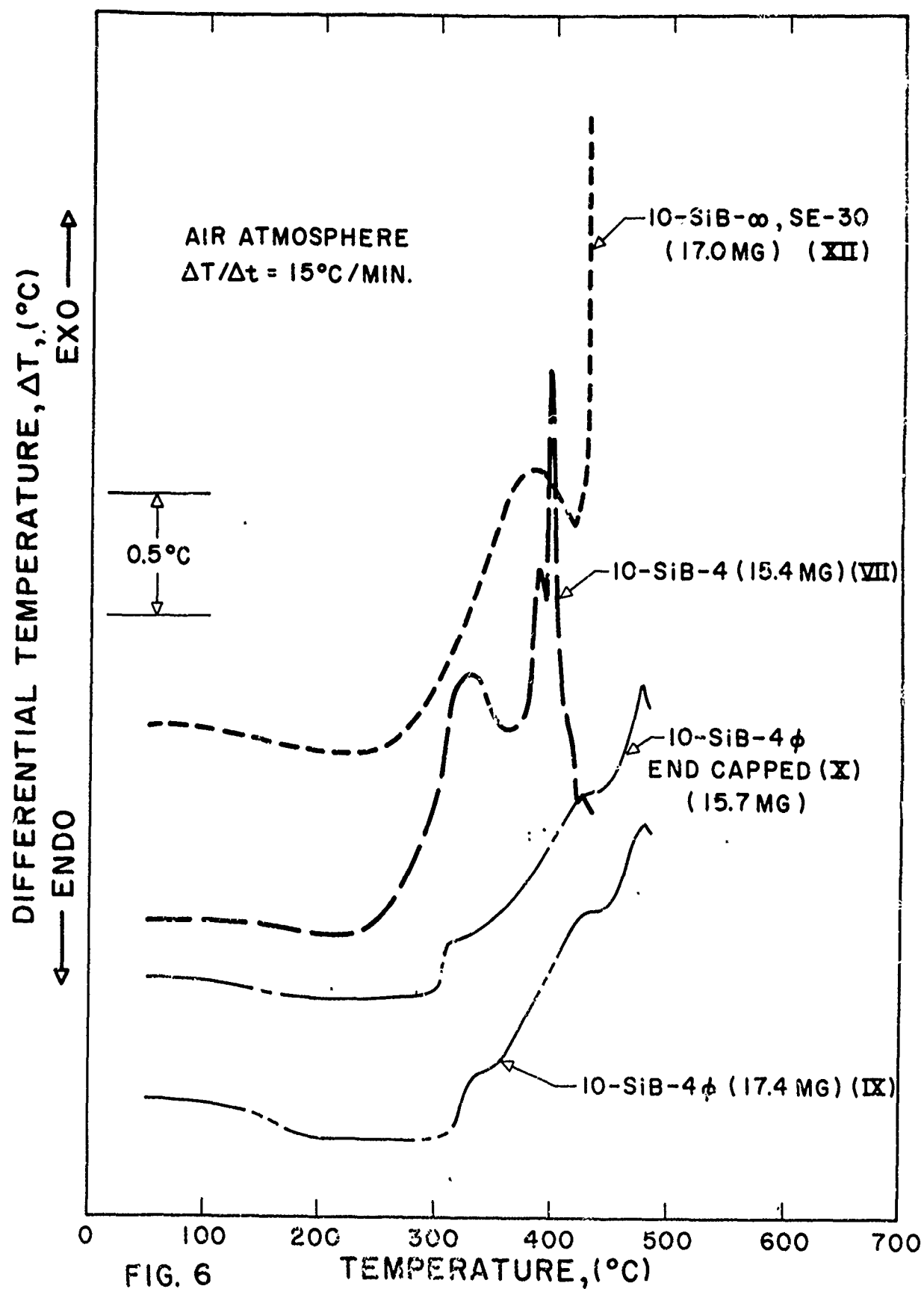


FIG. 6